Journal of Fluorine Chemistry 143 (2012) 220–225

Contents lists available at SciVerse ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Reaction of hexafluorothioacetone dimer with ketene dimethylacetal and dimethyl thioacetal

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ARTICLE INFO

Article history:
Received 10 April 2012
Received in revised form 19 June 2012
Accepted 27 June 2012
Available online 6 July 2012

Keywords:
2,2,4,4-Terakis(trifluoromethyl)dithienane-1,3
1,1-Dimethoxy ethylene
Ketene dimethoxyacetal
2,2-Bis(trifluoromethyl)-3,3-bis(methoxy)thietane
2,2-Bis(trifluoromethyl)-4,4-bis(methoxy)thietane

ABSTRACT

It was demonstrated that the fluoride anion catalyzed reaction of 2,2,4,4-terakis(trifluoromethyl)-dithienane-1,3 (**1**, cyclic dimer of hexafluorothioacetone) with ketene dimethylacetal (**2**, 1,1-dimethoxy ethylene) leads to the formation of 2,2-bis(trifluoromethyl)-3,3-bis(methoxy)thietane (**3**), rather than expected 2,2-bis(trifluoromethyl)-4,4-bis(methoxy)thietane isomer (**4**). Compound **3** is a kinetic product and upon storage at ambient temperature undergoes quantitative isomerization into **4**. The isomerization proceeds through the formation of free hexafluorothioacetone, which was trapped as cycloadduct with quadricyclane. It was also demonstrated that the ethylene **2** is able to react with dimer **1** in the absence of the catalyst. The reaction results in unusual ring opening process producing (2,2-dimethoxyvinyl)(1,1,1,3,3,3-hexafluoro-2-(1,1,1,3,3,3-hexafluoropropan-2-yl)thio)propan-2-yl)sulfane (**11**).

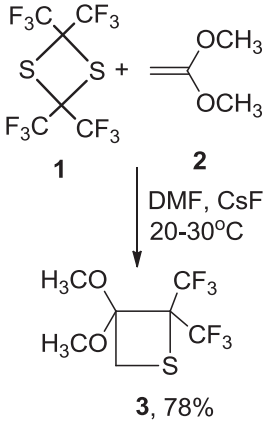
1. Introduction

The reaction of electron-rich olefins with hexafluorothioacetone (HFTA) was first reported by Middleton [1]. Since this pioneering work, a large number of the corresponding [2 + 2] cycloadducts have been prepared using the fluoride anion catalyzed reaction of hexafluorothioacetone dimer – 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane (**1**) with vinyl ethers [2,3]. Although at this point, there is no reasonable explanation in the literature of the regiochemistry observed in this reaction, the structure of the corresponding cycloadducts – 4-alkoxy-2,2-bis(trifluoromethyl)thietanes – was firmly established [3,4], leaving no doubt of highly regio-selective nature of this [2 + 2] cycloaddition process, which leads to exclusive formation of the thietanes bearing –OR (or –SR group) in an α-position to sulfur. The same regiochemistry was also observed in recently reported reaction of styrenes carrying p-donors in *para*-position [5].

In this study, it was found that the reaction of **1** with ketene dimethylacetal (1,1-dimethoxy ethylene, **2**) catalyzed by fluoride anion, deviates significantly from previously reported results, unexpectedly leading to the formation of 2,2-bis(trifluoromethyl)-3,3-dimethoxy)-thietane (**3**). Compound **3** is kinetic product and at ambient temperature it undergoing the isomerization into 2,2-bis(trifluoromethyl)-4,4-bis(methoxy)thietane (**4**).

2. Results and discussion

It was found that the CsF- catalyzed reaction of **1** with 1,1-dimethoxy ethylene **2** gave unexpected result – contrary to reported examples of the reaction of vinyl ethers HFTA dimer (**1**), the reaction between **1** and **2** leads to the formation of thietane **3**, rather than expected product **4** (see Eqs. (1) and (2)).



(1)

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[1] Publication No. 2012-546.

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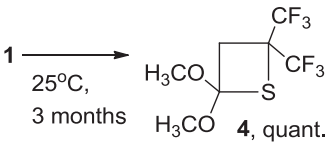
http://dx.doi.org/10.1016/j.jfluchem.2012.06.031

Compound **3** was isolated by distillation under reduced pressure. The structure was assigned based on combined of ^{1}H, ^{19}F, and ^{13}C NMR, IR-spectroscopy, and mass-spectrometry data. Unexpectedly, it was found, that upon storage at ambient temperature compound **3** underwent clean isomerization into the isomer **4**. Although this reaction was rather slow (3 months at 25 °C), it led to quantitative formation of 2,2-bis(trifluoromethyl)-4,4-bis(methoxy)thietane (**4**).



(2)

Based on this observation, the conclusion was made that in the CsF catalyzed reaction between **1** and **2**, the compounds **3** and **4** are the kinetic the thermodynamic products, respectively.

In sharp contrast to **3**, which is a liquid at ambient temperature and does not undergo crystallization even at −50 °C, isomer **4** is a low-melting crystalline solid (m.p. 28–28.5 °C). The structure of this material was confirmed by single crystal X-ray diffraction (Fig. 1).

Both isomers have very similar ^{1}H NMR spectra and an absence of H–F coupling in NMR of both compounds makes the extraction of structural information challenging. The major difference in the ^{19}F spectra is the substantial upfield shift of singlet resonance $-CF_3$ groups in compound **3** (−66.04 vs. −72.76 ppm for **4**, Table 1), which is believed to be caused by steric deshielding of CF_3 groups by two methoxy groups. A similar trend was observed earlier in cycloadducts of HFTA with quadricyclane and 1,3-cyclohexadiene, where more sterically hindered *exo*-oriented CF_3 group was always shifted upfield compared to the *endo*-oriented CF_3 [6]. Similarly, differences in chemical shifts of the carbon bearing two CF_3 groups were observed in ^{13}C NMR spectra of **3** and **4**. The chemical shift of the resonance of this carbon in **4** (δ = 43.87 ppm) appeared in a region typical of 4-alkoxy-2,2-bis(trifluoromethyl)-thietanes (δ = 43–46 ppm, sept.) [3], while the resonance of this carbon in **3** was shifted down field by >20 ppm (δ = 65.10 ppm).

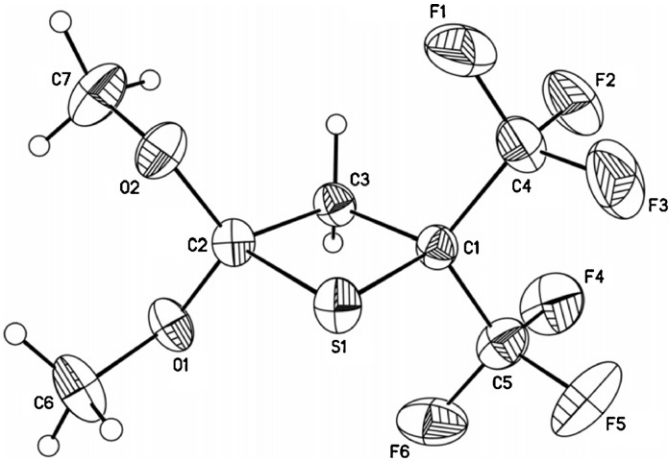
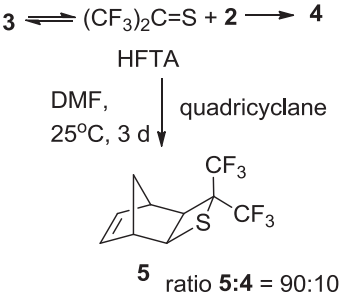


Fig. 1. Crystal structure of **4**. Thermal ellipsoids drawn to the 50% probability level.

It should be pointed out that the isomerization of **3** into **4** involves a cyclo-reversion process with generation of free HFTA (Eq. (3)), which was intercepted when quadricyclane (an efficient trap for HFTA [6]) was added to the solution of **3** in DMF. The formation of the known cycloadduct **5** [6] as major product was observed in this process, along with smaller amount of isomer **4** (Eq. (3)).



(3)

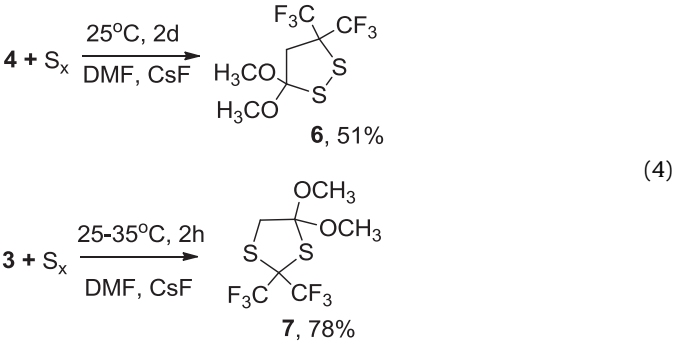
Compounds **3** and **4** not only have different physical properties, but also rather different chemical behaviors. For example, the

Table 1
Data of ^{1}H, ^{19}F and ^{13}C NMR spectroscopy and MS spectrometry for new materials.

Entr. no.	Compound no.	^{1}H NMR[a] (δ, ppm, J, Hz)	^{19}F NMR[a] (δ, ppm, J, Hz)	^{13}C NMR[a,b] (δ, ppm, J, Hz)	MS (m/z)
1	**3**	3.35 (6H, s), 3.46 (2H, s)	−66.04	34.39, 48.31, 65.10 (sept., 28.5),102.61, 122.56 (q, 273)	270 (M^+, $C_7H_8F_6O_2S^+$)
2	**4**	3.34 (2H, s), 3.38 (6H, s)	−72.76	41.54 (sept, 1.6), 43.87 (sept., 32.7) 50.86, 106.57, 124.20 (q, 282)	270 (M^+, $C_7H_8F_6O_2S^+$)
3	**6**	3.38 (2H, s), 3.46 (6H, s)	−70.56	42.89, 52.13, 66.12 (sept., 27.6), 124.09 (q, 285), 127.43	302 (M^+, $C_7H_8F_6O_2S_2^+$)
4	**7**	3.45 (2H, s), 3.46 (6H, s)	−70.33	42.06, 52.68, 67.00 (sept., 32.5), 123.80 (q, 282), 129.16	302 (M^+, $C_7H_8F_6O_2S_2^+$)
5	**8**	3.82 (3H, s), 5.61 (1H, d, 4.2)	−59.14 (3F, d, 18.1), −119.58 (1F, qd, 18.1, 4.2)	56.70, 84.38, 104.62 (qd, 36.5, 5.3), 120.56 (qd, 270,3.4),150.49 (m, 2.0), 164.31 (d, 299.0)[c]	200 (M^+, $C_6H_4F_4OS^+$)
6	**10**	2.12 (2H, s) 3.38 (6H, s)	−72.42	14.68, 42.18 (sept, 1.3), 42.33 (sept., 32.9) 61.32, 122.87 (q, 280)	302 (M^+, $C_7H_8F_6S_3^+$)
7	**11**[d]	3.76 (3H, s), 3.77 (3H, s), 3.98 (1H, s), 4.64 (1H, sept, 7.2)	−65.31 (6F, m), −66.02 (d sept., 7.2, 2.6)	50.15, 50.15 (sept. 32.6), 54.84, 55.62.0, 56.64, 66.15 (sept., 28.0), 122.42 (q, 286.0), 123.12 (q, 286.0), 169.08	452 (M^+, $C_{10}H_8F_{12}O_2S_2^+$)
8	**12**[e]	3.79 (5H, m), 4.46 (1H, sept, 7.6)	−64.97 (6F, m), −65.84 (6F, m)	33.46, 50.18 (sept, 31.8), 53.16, 65.07 (sept, 3.0), 67.01, 122.0 (q, 282.0), 122.73 (q, 289.0), 167.17	438 (M^+, $C_9H_6F_{12}O_2S_2^+$)
9	**13**	3.32 (11H, s), 4.51 (1H, sept., 7.5)	−65.17 (6F, m), −65.94 (6F, m)	–	452 ($M-CH_3OH)^+$, $C_{10}H_8F_{12}O_2S_2^+$)

[a] In $CDCl_3$ solvent.
[b] $^{13}C\{H\}$ NMR.
[c] ^{13}C NMR: 56.69 (q, J = 143 Hz), 84.38 (d, J = 189.0 Hz), 104.60 (qt, J = 36.5, 5.2 Hz), 120.56 (qdd, J = 270, 3.4, 1.8 Hz), 150.49 (d quint., J = 3.8, 2.0 Hz), 164.31 (ddq, J = 299.0, 10.2, 3.3 Hz) ppm.
[d] IR (in CH_2Cl_2): 1592 (C=C) cm^{-1}.
[e] IR (neat): 1747 (C=O) cm^{-1}.

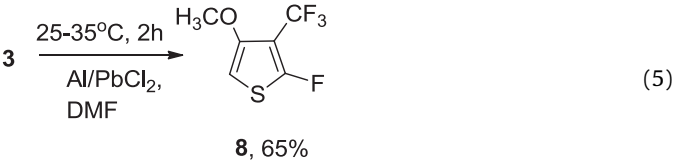
CsF-catalyzed reaction of **4** with sulfur leads to the expected 3,3-dimethoxy-5,5-bis(trifluoromethyl)-1,2-dithiolane (**6**, Eq. (4))., while similar reaction of freshly prepared **3** led to the formation of 4,4-dimethoxy-2,2-bis(trifluoromethyl)-1,3-dithiolane (**7**, Eq. (4)). The structure of this material was confirmed by single crystal X-ray diffraction.



(4)

The formation of dithiolane **7** is consistent with the presence of free HFTA in equilibrium with **3** (see Eq. (3)), since we demonstrated recently that, in the presence of sulfur, HFTA (generated "*in situ*" from dimer **1**) reacts with vinyl ethers producing the corresponding 4-alkoxy-2,2-bis(trifluoromethyl)-1,3-dithiolanes [3].

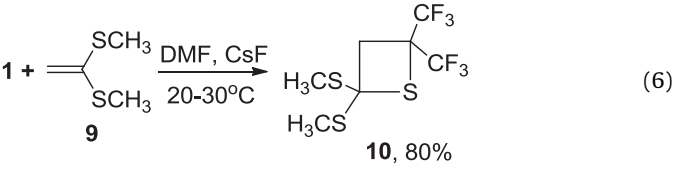
Isomer **3** also undergoes reductive ring expansion in the presence of activated aluminum powder. However, in contrast to 4-alkoxy-2,2-bis(trifluoromethyl)thietanes giving the corresonding dihydrothiophenes [4], this reaction produced the thiophene **8** (Eq. (5)).



(5)

The proposed structure of **8** is supported by the ^{1}H, ^{19}F and ^{13}C NMR spectroscopy and mass spectrometry data.

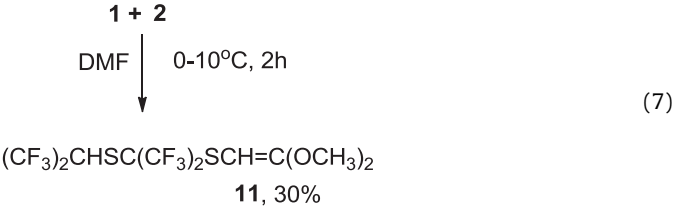
It should be pointed out that the sulfur analog of olefin **2** – the compound **9** – has a different reactivity, and the reaction with **1** led to exclusive formation of the expected product **10** (Eq. (6)). Monitoring of the reaction by NMR confirmed the absence of other isomer in the reaction mixture.



(6)

The structure of **10** was confirmed by single crystal X-ray diffraction (Fig. 2).

The temperature and catalyst have a very pronounced effect on the outcome of the reaction of **2** and **1**. The reaction carried out in DMF at 0 °C, or at ambient temperature in the absence of the catalyst, led to the predominant formation of product **11**, which was isolated after crystallization from hexane.



(7)

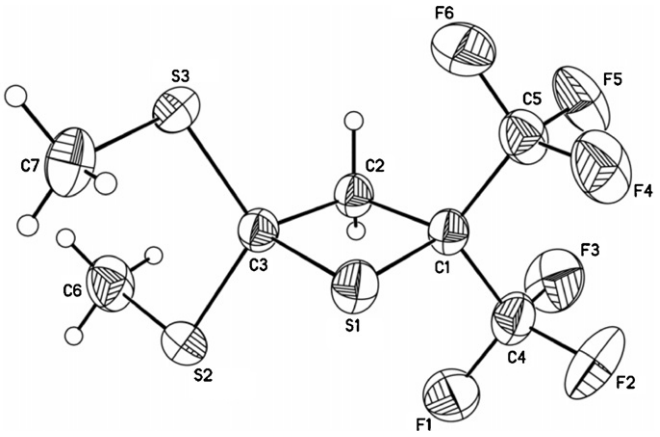
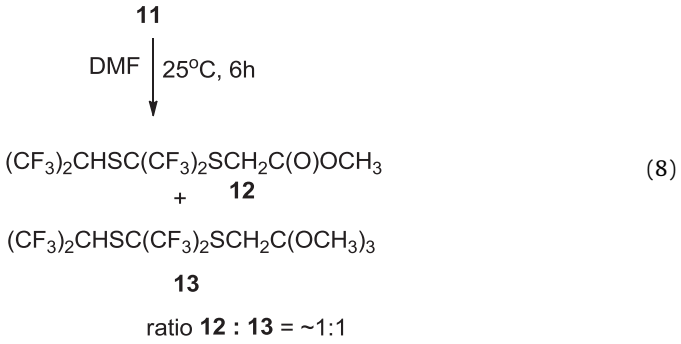


Fig. 2. Crystal structure of **10**. Thermal ellipsoids drawn to the 50% probability level.

Compound **11** was fully characterized by NMR spectroscopy and the structure was confirmed by single crystal X-ray diffraction (Fig. 3).

The initial reaction, especially at low temperature, leads to exclusive formation of **11** (NMR). However, this material is not stable, and at ambient temperature in DMF solvent it slowly undergoes conversion to a mixture of products **12** and **13**.



(8)

Ortho ether **13** was isolated by crystallization of the fraction obtained by vacuum distillation of the crude reaction mixture (see Section 2), and its structure was established by X-ray diffraction.

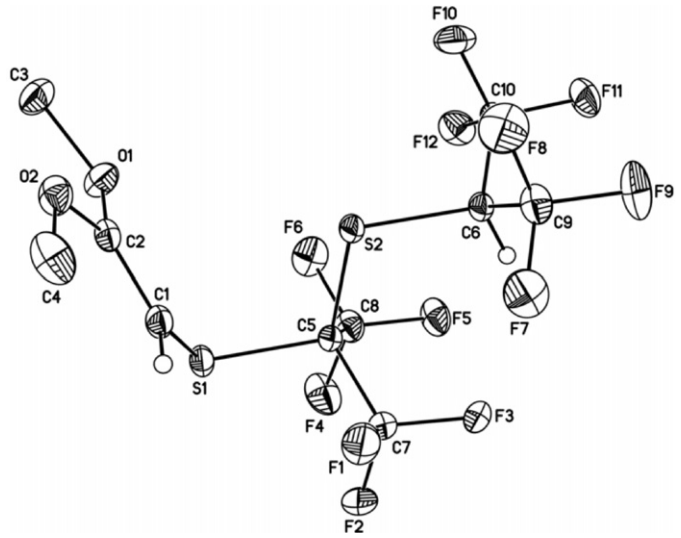
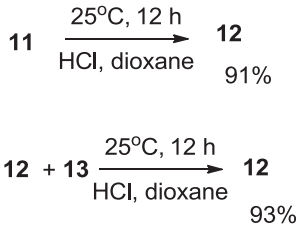


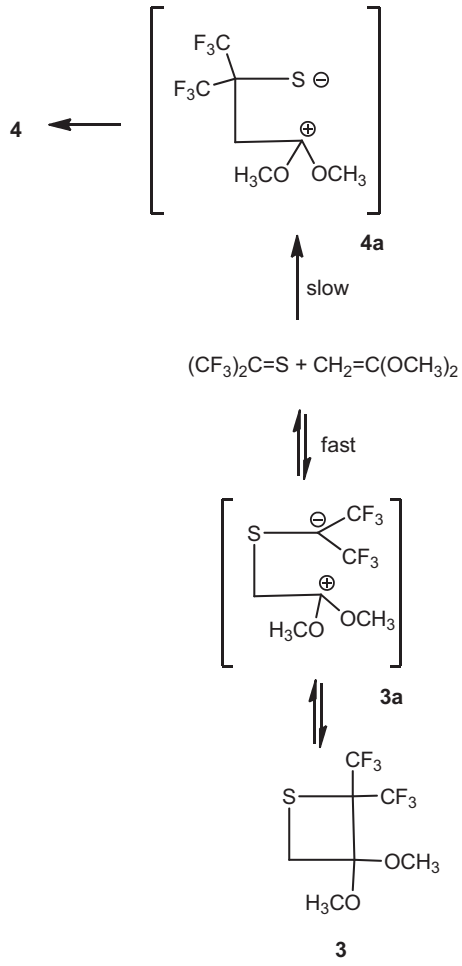
Fig. 3. Crystal structure of **11**. Thermal ellipsoids drawn to the 20% probability level. The methoxy groups hydrogen atoms have been omitted for clarity.

Compound **12** was prepared independently, by acidic hydrolysis either compound **11** or the mixture of **12** and **13** (Eq. (9)).



(9)

The mechanism of the formation of compound **3** in the reaction of **1** and **2** presents an interesting problem. Indeed, why does compound **3** form in this process, while the formation of this regioisomer was never observed in the reaction of vinyl ethers (alkoxy ethylenes) and **1** [1–3]? And why compound **3** forms in this process at all? One possible explanation presented in Scheme 1 is based on the assumption that the formation of intermediate zwitterion **3a** (leading to the compound **3** after cyclization) is relatively fast due to a lower activation energy for this process. However, steric repulsion between $-OCH_3$ and $-CF_3$ groups in the product **3** leads to elongation of the $(CF_3)_2C-C(OCH_3)_2$ bond, enhancing reversed process – ring opening and subsequent formation of HFTA and **2**. The presence of free HFTA in this process was demonstrated in a trapping experiment, using quadricyclane (Eq. (3)). Although the activation energy for the formation of intermediate **4a** is higher (due to less efficient stabilization of zwitterion **4a** compared to **3a**), due to lower ring strain and lack of steric repulsion between the $-CF_3$ and $-OCH_3$ groups compound **4** is more stable thermodynamically. Although the process for the formation of **4** is much slower, it is not reversible, leading to quantitative formation of **4**. The absence of the isomer structurally similar to **3** in the reaction of HFTA with ketene dimethylthioacetal **9** (Eq. (6)) is consistent with this mechanism, since this isomer should be significantly destabilized, due to steric repulsion between larger $-SCH_3$ (compared to OCH_3) and $-CF_3$ groups.



Scheme 1. Mechanism of formation of thietanes **3** and **4**.

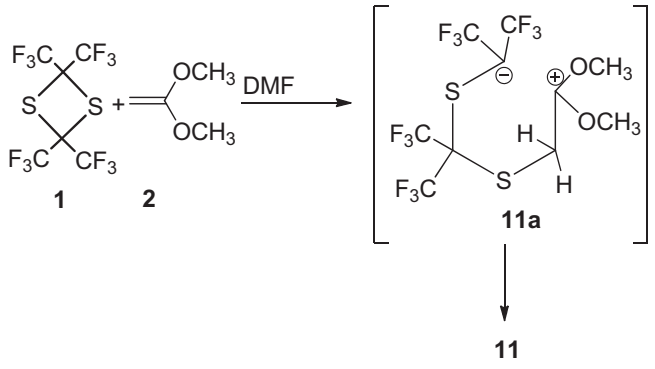
It should be pointed out, that similar process – reversible formation of the corresponding cyclobutanes in the reaction of tetracyanoethylene and alkyl vinyl ethers – was previously reported by Huisgen, and the formation of a zwitterion intermediate in this process was unambiguously supported by experimental data [7,8].

The mechanism of the formation of zwitterion **3a** is not exactly clear at this point. It can be formed as the result of "nucleophilic" attack of **2** on the sulfur of HFTA by the CH_2-terminus (vs. "electrophilic" attack of HFTA on $-CH_2$ group of **2**, leading to the formation of isomeric zwitterion **4a**). Indeed, some reactions of HFTA with "soft" nucleophiles have been reported to occur through the attack on sulfur [9]. The ethylene **2** is known to be highly nucleophilic and it was reported to react with electron-deficient materials such as carbonyl compounds [10], diazopyrazoles [11] and acetylenic esters [12]. These reactions rapidly proceed at ambient temperature and in the absence of a catalyst. For example, for the [2 + 2] cycloaddition reaction between chloral and **2** in $CDCl_3$ the $t_{1/2}$ was reported to be less than 1 min at 25 °C [10].

Alternative mechanism, responsible for the formation of **3a**, can involve a single electron transfer process, leading to the formation of a $[\mathbf{2}]^{\bullet+}$ $[HFTA]^{\bullet-}$ pair, followed by coupling through two radical termini ($-CH_2^{\bullet}$ and $-S^{\bullet}$).[2] Although we were not able to find reported value of ionization potential (IP) for compound **2**, it is known that the introduction of a methoxy group decreases the IP of ethylene by 1.53 eV (IP = 8.93 eV for $CH_2{=}CHOCH_3$ vs. 10.51 eV for $CH_2{=}CH_2$) [13], so it is reasonable to believe that the introduction of second CH_3O- will further lower the IP of **2**, increasing the ability of **2** to donate an electron.

However, at this point there are not sufficient data to choose between these two mechanisms.

The mechanism of noncatalyzed reaction between **1** and **2** is presented in Scheme 2. Since this reaction was carried out in the absence of the catalyst (so, monomeric HFTA was not present in the reaction system), we believe that this process starts with nucleophilic attack of **2** by CH_2- termini on the positively charged sulfur of **1**.



Scheme 2. The mechanism of the reaction compounds **1** and **2** in the absence of the catalyst.

[2] One of the reviewers suggested the utilization of electron-transfer inhibitors to determine, if this will affect the rate of formation of compound **3**.

The intermediate zwitterion **11a** undergoes intramolecular transfer of a proton to the carbanion center, resulting in the formation of unsaturated product **11**. It should be pointed out that an alternative mechanism of formation **11**, involving a single electron transfer process also cannot be ruled out at this point.

3. Experimental

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker DRX-500 (499.87 MHz) instrument using $CFCl_3$ or TMS as internal standards in $CDCl_3$ as a lock solvent. GC and GC/MS analyses were carried out on a HP-6890 instrument, using an HP FFAP capillary column and either TCD (GC) or mass selective (GS/MS) detectors, respectively. Dry DMF (99.8%, water – 100 ppm), 1,1-dimethoxyethylene (ketene dimethylacetal, **2**, assay 95.5%), 4 M solution of HCl in 1,4-dioxane (Aldrich), aluminum powder (200 mesh, 99%, Aldrich), sublimed sulfur (Alfa-Aesar, 99.5%), 1,1-bis (methylthioethylene) (ketene dimethylthioacetal (**9**), TCI America), and quadricyclane (Exciton, 98%, remainder norbornadiene) were obtained from commercial sources and used without further purification. CsF (Aldrich) was dried at 100–120 °C under dynamic vacuum for 4–8 h and was stored and handled inside a glove box. Compound **1** was prepared according to a modified procedure using CsF as a catalyst [3]. Compound **5** was identified by comparison of NMR data to previously reported values [6]. Due to a high ratio of sulfur to fluorine, elemental analysis were not attempted for new materials, and the purity of all isolated compounds established by GC and NMR spectroscopy was at least 98%.

3.1. Crystallography

X-ray data for **4**, **7**, **10**, **11** and **13** were collected at −100 °C using a Bruker 1K CCD system equipped with a sealed tube molybdenum source and a graphite monochromator. The structures were solved and refined using the Shelxtl [14] software package, refinement by full-matrix least squares on F^2, scattering factors from Int. Tab. Vol. C Tables 4.2.6.8 and 6.1.1.4. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC #799785–799790. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

3.1.1. Preparation of *3*

Method A: The solution of **1** in DMF was prepared using the procedure described in Ref. [3], by bubbling 33 g (0.21 mol) of hexafluoropropylene into a mixture of 200 ml of dry DMF, 6.4 g of sulfur and 1.0 g (0.0065 mol) of dry CsF at 50–65 °C. After all the sulfur dissolved, the reaction mixture was cooled to 25 °C, and 17 g (0.19 mol) of **2** was added slowly keeping the internal temperature of the reaction mixture <35 °C. After all of **2** was added, the reaction mixture was agitated for 1 h, diluted by 500 ml of water, and extracted by hexane (100 ml × 3). The combined organic layers were washed by water (200 ml × 3), dried over $MgSO_4$, and then the solvent was removed under vacuum. The crude product **3** (50 g, purity 98%, containing 2% of isomer **4**, NMR) was distilled under vacuum to give 41 g (80%) of **3**, b.p. 39–41 °C/2 mm Hg. Data of NMR spectroscopy and mass spectrometry for **3** are given in Table 1.

Method B: Compound **2** (8.5 g, 0.096 mol) was added slowly to a mixture of **1** (18.2 g, 0.05 mol) and 1 g (0.0065 mol) of dry CsF at 25–35 °C. The isolation of **3** was carried out as described in Method A. After vacuum distillation, 42 g (82%) of compound **3** was isolated.

3.1.2. Preparation of *4*

Clear, liquid compound **3** (27 g, 0.1 mol, purity >99%, NMR) stored in glass sample vial crystallized over a three month period at ambient temperature. According to NMR, the solid product was compound **4** (purity >99%), m.p. 28–28.5 °C, yield quantitative. Data of NMR spectroscopy and mass spectrometry for **4** are given in Table 1.

3.1.3. The reaction of *3* with quadricyclane

The solution of 3.6 g (0.013 mol) of **3** and 2 g (0.022 mol) of quadricyclane in 15 ml of dry DMF was kept in a glass sample vial at ambient temperature. The progress of the reaction was monitored by ^{1}H and ^{19}F NMR spectroscopy. The conversion of **3** was 32% (4 h), 70% (24 h), and 93% (48 h). After 72 h, the reaction was complete, and the reaction mixture contained compounds **5** and **4** in a 9:1 ratio (NMR).

3.1.4. Preparation of *6*

A mixture of 5.4 g (0.02 mol) **4**, 0.64 g (0.02 mol) of sulfur, 0.1 g (0.0007 mol) dry CsF, and 20 ml of dry DMF was agitated for 2 days at 25 °C. The reaction mixture was diluted with 50 ml of water, and extracted by hexane (30 ml × 3). The combined organic layers were washed with water (30 ml × 3), dried over $MgSO_4$, and then the solvent was removed under vacuum. The crude product (orange oil, 3.1 g, purity 96%) was identified as compound **6**. No further purification of **6** was attempted. Data of NMR spectroscopy and mass spectrometry for **6** are given in Table 1.

3.1.5. Preparation of *7*

After compound **3** (0.09 mol) was generated in 200 ml of DMF as described in Ref. [3], and its formation was confirmed by NMR, 3.2 g of sulfur was added to the reaction mixture (mildly exothermic). The reaction mixture was agitated at ambient temperature for 12 h, and then it was diluted with 500 ml of water, and extracted with hexane (100 ml × 3). The combined organic layers were washed with water (100 ml × 3), dried over $MgSO_4$, and then the solvent was removed under vacuum. The crude product was distilled under vacuum to give 23 g (78%) of **7**, b.p. 65–67 °C/1.7 mm Hg, which crystallized on standing. Data of NMR spectroscopy and mass spectrometry for **7** are given in Table 1.

3.1.6. Preparation of *8*

A solution of compound **3** (5.7 g, 0.021 mol) in 10 ml of dry DMF was slowly added to a mixture of 1 g of Al powder activated by 0.2 of $PbCl_2$ (see Ref. [4] for activation procedure) in 750 ml of dry DMF at a rate sufficient to keep the internal temperature <35 °C. The reaction mixture was agitated for 2 h at ambient temperature, filtered, diluted with 200 ml of water, and extracted with hexane (50 ml×). The combined organic layers were washed with water (100 ml × 3), dried over $MgSO_4$, and then the solvent was removed under vacuum. The crude product was distilled under vacuum to give 2.8 g (65%) of **8**, b.p. 86–89 °C/50 mm Hg. Data of NMR spectroscopy and mass spectrometry for **8** are given in Table 1.

3.1.7. Preparation of *10*

A solution of compound **9** (1.2 g, 0.01 mol) was added slowly to a mixture of 1.9 g (0.0052 mol) of **1** and 0.1 g (0.0007 mol) of dry CsF at 25–28 °C. The reaction mixture was agitated at ambient temperature for 3 h, and then worked up as described above to give 2.4 g (80%) of slightly brown solid, m.p. 34–36 °C, identified as compound **10** (purity 98%) by NMR.

3.1.8. Preparation of *11*

To a solution of 10 g (0.028 mol) of **1** in 30 ml of dry DMF was slowly added a solution of 2.5 g (0.028 mol) of **2** in 5 ml of DMF at 0–2 °C over ~5 min. The reaction mixture was agitated at 2 °C for

15 min, and then the solvent was removed completely under vacuum (1–01 mm Hg, 20–25 °C). The crude reaction mixture was crystallized from hexane at −20 °C, and 3.5 g (yield 30%) of white crystalline compound **11** was isolated. M.p. 58–59 °C. Data of NMR spectroscopy and mass spectrometry for **11** are given in Table 1.

*3.1.9. Preparation of **12***

1.5 g (0.033 mol) of **11** was dissolved in 12 ml of a 4 M solution of HCl in 1,4-dioxane. The reaction mixture was kept at ambient temperature for 12 h. The solvent was removed under reduced pressure to leave 1.4 g of a clear oil, identified as ester **12** (NMR, purity >98%), calculated yield 91%. Data of NMR spectroscopy and mass spectrometry for **12** are given in Table 1.

Similarly, 5 g of a mixture of **12** and **13** (ratio 1:1) was treated with 30 ml of a 4 M solution of HCl in 1,4-dioxane for 16 h at 25 °C, and 4.8 g (calculated yield 93%, purity 97%, NMR) of compound **12** was isolated.

*3.1.10. Preparation of **13***

A mixture of 2.8 g of **2** (0.03 mol) and 11 g (0.03 mol) of **1** in 20 ml of THF was kept at ambient temperature for 7 days. It was diluted with 100 ml of water, extracted with hexane (30 ml × 3), washed with water (100 ml × 3), and then the organic phase was dried over $MgSO_4$. The solvent was removed under vacuum and the residue was distilled under reduced pressure to give 4.8 of a fraction with a b.p. 55–58 °C/0.5 mm Hg. This fraction partially crystallized on standing. It was filtered and solid was recrystallized form hexane to give 1.8 g (13%) of compound **13** (purity 96%, NMR). Data of NMR spectroscopy and mass spectrometry for **13** are given in Table 1.

Acknowledgments

Authors are grateful to Dr. C. Junk for helpful discussions and suggestions, Karin Karel for manuscript proofreading and Timothy Bentz for technical support.

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